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## Technical Memorandum

To	Steve Way/US EPA	Page	1 of 6
CC	Tony Brown/AR; Chuck Stilwell/AR; Terry Moore/AR; Steve Dischler/AR; Sandy Riese/EnSci; Chris Sanchez/AECt		
Subject	Rico-Argentine Mine Site - Rico Tunnels Operable Unit OU01 Investigation of Calcareous Sludge Pore Fluid on Leachability of Calcine Tailings		
From	Douglas M. Yadon, PE/AECOM		
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### Background and Objectives

Temporary dewatering cells are being constructed over calcine tailings in the Pond 16/17 area at the St. Louis Ponds site of the Rico Tunnels Operable Unit OU01. These tailings are of relatively low permeability and limited fluids will be available for leaching; however, EPA requested in their review of the Initial Solids Removal Plan (ISRP; Atlantic Richfield Company, 2011) that the effect of higher pH leaching fluids on potential changes in arsenic (As) and selenium (Se) concentrations be evaluated. The alkaline pH solution would result from calcium carbonate saturated pore fluids originating from the dewatering sludges from Ponds 15 and 18. Some of the calcine tailings have solid phase calcite (calcium carbonate) present in the mineral matrix (see ISRP Appendix C), as well, and no significant change in solution chemistry would be expected due to calcium carbonate. If the calcine tailings have a less alkaline pH, however, limited changes in As and Se concentrations potentially could occur. In order to evaluate this possibility a procedure was developed to measure changes in the pH and concentration of metals, As and Se in particular, in pore fluids of calcine tailings when calcareous fluids from dewatering Pond 15/18 sludges are introduced. Solids from the calcine tailings will also be described and physical properties determined to estimate the magnitude of leaching that might be expected through these tailings.

### Sampling

Calcine tailings deposits will be sampled from three depth intervals at two locations within the Ponds 16/17 area. The first location selected for sampling is near the north end of the calcine tailings adjacent to monitoring well GW-5 and the adjacent boring EB-1 where the tailings are near the estimated maximum thickness and groundwater is shallower than in areas further south in the Pond 16/17 area. The second location is near boring DH-11 in the center of the Pond 16 area. At the first location two samples will be taken above the water table where previous microprobe results suggest that calcite is absent or only a minor constituent; the third sample will be taken below the water table where the microprobe data suggest that calcite is an abundant constituent. At the second location a sample will be

taken in the approximate upper third of the tailings above the water table where microprobe results suggest that calcite is absent or only present as a minor constituent. The middle sample will be taken in what is estimated to be the zone of seasonal groundwater fluctuation. The lower sample will be taken below the groundwater table.

A tracked excavator with an effective digging reach of 25 feet (Caterpillar 330) will be used to retrieve bulk samples of calcine tailings at the two sampling locations. The tracked excavator bucket will be decontaminated prior to collecting the bulk sample at each of the three targeted depth intervals at each location. Care will be taken to avoid mixing of material from higher in the excavation with the sample to be taken at a given depth interval. Safety precautions will be implemented in the operation of the equipment and to preclude unauthorized access to the sampling area.

Calcine tailings samples will be described visually, including standard geotechnical soils description, and tested for reaction using 10% HCl for effervescence. Samples of calcine tailings with a positive effervescence and containing calcium carbonate (usually below the groundwater table) already have pH values between 7 and 8. For this reason it is expected that leaching calcine tailings with Pond 15/18 treatment sludge pore water (pH buffered to near 8 by calcium carbonate) will have little effect on solution chemistry. At least three of the six calcine tailings samples will be targeted to be taken from non-calcareous zones based on the microprobe results reported in Appendix C of the ISRP and as confirmed by the field HCL effervescence testing noted above. Two of the samples will be taken below the water table at a depth interval within which the microprobe results identified abundant calcite in the samples. Soil samples will be collected in 16 oz glass jars. Care will be taken to pack soils into the jars to minimize airspace. Care will also be taken to ensure that the jar rim is clean and that a tight seal is made with the lid to minimize aeration of the samples. Calcine tailings samples will be kept on ice, at 4°C or less, during transport to the laboratory.

Samples of pore fluid will be collected from saturated calcareous sludges from the existing Pond 18 and/or Pond 15. This will be accomplished using porous cup lysimeters. The fluid will be extracted using a vacuum and 2 L of solution per calcine tailings sample tested will be collected, placed in plastic containers, and transported to the laboratory at 4°C.

### **Laboratory Analyses**

The calcine tailings samples will be analyzed at Pace Analytical Laboratories using the Synthetic Precipitation Leaching Procedure (SPLP), EPA Method 1312. Two leaching solutions will be utilized: 1) the standard western SPLP leaching solution; and 2) unamended calcareous pore fluid collected in the field from calcareous sludges in existing Ponds 18 and/or 15. The leaching events will utilize Zero Headspace Extraction (ZHE) devices to minimize oxidation due to equilibration with laboratory air during the extraction period.

### **Modified EPA Method 1312 (SPLP)**

The SPLP (USEPA Method 1312; USEPA, 1986; 1994 update) is a method designed to evaluate the impact of contaminated soils on groundwater. The extraction fluid consists of slightly acidified de-ionized water that is formulated to simulate natural precipitation. A mixture of 60/40 H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> (by weight) is used to achieve the approximate pH for the

extraction fluid. The pH of the de-ionized water is adjusted with the 60/40 H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> mixture, depending on which side of the Mississippi River the materials originate from, to either 4.2 (+/-) 0.05 (east of the Mississippi) or 5.0 (+/-) 0.05 (west of the Mississippi).

The SPLP extraction method for 100% solids and no volatiles will be used for this study. A sample that is 100% solids requires reduction of particle size to <1 cm (if necessary), and extracting the solid at a 20:1 ratio (100 g of mine waste to composite material / 2,000 g extraction fluid) on an end-over-end rotary agitator for 18 hours. The solid/liquid slurry is then filtered through a -0.7 µm borosilicate glass fiber filter utilizing a pressure filtration unit.

For this study, the pH 5.0 extraction fluid will be used as well as pore fluids from the calcareous sludges. There is not anticipated to be a need for particle size reduction of the calcine tailings based on descriptions of these materials in previous exploratory drilling and test pit logs at the Pond 16/17 site as fine to very fine grained silty sand.

Clean extraction vessels (Nalgene® high-density polyethylene 2-liter bottles) will be used. One hundred grams of each sample will be weighed and placed in the extractor vessel along with two liters of pH 5.0 extraction solution or pore fluid, as appropriate. Teflon® tape will be used to wrap the bottle threads to create a tight seal. The extractor vessels will be secured in an Analytical Testing Rotary Agitator and rotated end-over-end for eighteen hours at approximately thirty revolutions per minute.

Following extraction, the samples will be filtered through 0.7 µm borosilicate glass fiber filter (Gelman Sciences Inc. P/N 66257, TCLP glass fiber filter). The filtration unit to be used is a Gelman Sciences Hazardous Waste pressure filtration unit. The filters will be placed in position and acid washed with 1 liter of 1N HNO<sub>3</sub> followed by three one liter de-ionized water rinses prior to filtration of the samples. A small aliquot of the unfiltered leachate will be used for pH, DO and specific conductivity measurements. After filtration, aliquots of filtrate will be preserved for analysis.

When extraction is complete the following analysis will be completed for all samples.

**pH, Dissolved Oxygen, and Specific Conductivity:** The pH, DO and SC of all samples will be determined immediately upon removal from the ZHE device prior to filtration. Prior to initial use, the meters will be calibrated as needed with commercially available standards.

**Metals:** The SPLP solutions extracted will be filtered through a 0.6 to 0.8 µm filter and analyzed for Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mo, Ni, K, Se, Si, Ag, Na, Sr, Tl, V, and Zn using Inductively Coupled Plasma – mass spectroscopy (ICP-MS) and

for certain analytes Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Solution will be retained for other analysis if As and Se are below detection limits of ICP. If lower detection limits are required As and Se will be analyzed by Hydride Generation Atomic Absorption Spectroscopy. Preservation of the samples for metals analysis requires that the samples be filtered and acidified to pH <1.5 with Ultrapure HNO<sub>3</sub>. Maximum hold time is 180 days.

**Alkalinity:** Concentration of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> will be determined using titration endpoints.

**Ferrous Iron:** Ferrous iron will be determined using colorimetric techniques.

**Anions:** Sulfate, chloride, and fluoride will be determined using ion chromatography or equivalent methodology. Preservation of the samples for anion analysis requires filtration and refrigeration at 4°C. Samples will be analyzed within the hold time of 28 days.

### Quality Control

Table 1 below show the frequency and control limits of laboratory control checks to be used for leachate samples obtained from the leach experiments in this study. A brief description and definition of each type of quality control check follows. Results of the quality control checks will be presented.

Table 1 - Laboratory Quality Control Checks

<u>Quality Control Check</u>	<u>Frequency</u>	<u>Control Limits</u>
1. Preparation Blank	one per analytical batch	<IDL
2. Analytical Batch Duplicate	one per analytical batch	+/- 20% RPD
3. Reference Standards	one set per analytical grp	+20% RPD

**Preparation Blank:** A preparation blank is a sample of the appropriate volume of extraction fluid that is carried through the entire experimental procedure including analysis. The preparation blank is used to determine whether any added reagents, equipment, procedures, or processes introduce any contaminants to the samples. For laboratory studies, at least one preparation blank is run with each analytical batch.

**Analytical Batch Duplicates:** Analytical batch duplicates consist of two identical splits of a site composite that are carried through the entire experimental process, including analysis in order to determine the precision of the analytical results. For laboratory studies, at least one duplicate is run with each analytical batch.

**Reference Standards:** Water Standards will be submitted with each group of samples (by the lab) as a check on the analytical method. Standards for major cations and trace metals will be submitted with the sample groups for ICP-MS and ICP-AES analysis.

### References

Aflantic Richtfield Company. 2011. Initial Solids Removal Plan, Rico-Argentine Mine Site – Rico Tunnels Operable Unit OU01, Rico, Colorado: submitted to U.S. EPA Region 8. July 7.

U.S. Environmental Protection Agency. 1994. Test method for evaluating solid waste, physical / chemical methods (SW-846), 3<sup>rd</sup> edition, update 2B. Environmental Protection Agency, National Center for Environmental Publications, Cincinnati, OH 45268.

**Table 2 - Analytical Parameters  
Effects of Calcareous Leachate on Calcine Tailings**

PARAMETER	DETECTION LIMIT (MDL)	METHOD
<b>Unfiltered Samples</b>		
pH (s.u.)	+/- 0.01 pH	EPA 150.2
Temperature (°C)	+/- 1°C	Standard Method 2550
Electrical Conductivity (µmhos/cm)	+/- 2% Full Scale	EPA 120.1
Dissolved Oxygen	+/- 2% Full Scale	SM 4500-OG
<b>Filtered and Preserved Samples</b>		
<b>Non-Metals</b>		
Alkalinity (mg/L as CaCO <sub>3</sub> )	RL – 20 mg/L	EPA 310.1
Bicarbonate (mg/L as CaCO <sub>3</sub> )	2 mg/L	SM 2320
Carbonate (mg/L as CaCO <sub>3</sub> )	2 mg/L	SM 2320
Chloride (mg/L as Cl)	0.04 mg/L	EPA 300.0
Fluoride (µg/L as F)	0.02 mg/L	EPA 300.0
Hardness (mg/L as CaCO <sub>3</sub> )	RL – 0.5 mg/L	SM 2340 B
Total Dissolved Solids (mg/L as TDS)	RL – 5.0 mg/L	SM 2540C
Total Suspended Solids (mg/L as TSS)	RL – 5.0 mg/L	SM 2540D
Salinity	RL – 6 mg/L	SM 2510B (calculated)
Sulfate (mg/L as SO <sub>4</sub> )	RL – 1 mg/L	EPA 300.0
<b>Dissolved Metals</b>		
Aluminum (µg/L as Al)	2 µg/L	EPA 200.8
Antimony (µg/L as Sb)	0.07 µg/L	EPA 200.8
Arsenic (µg/L as As)	0.09 µg/L	EPA 200.8
Barium (µg/L as Ba)	0.08 µg/L	EPA 200.8
Beryllium (µg/L as Be)	0.02 µg/L	EPA 200.8
Boron (µg/L as B)	5.0 µg/L	EPA 200.7
Cadmium (µg/L as Cd)	0.03 µg/L	EPA 200.8
Calcium (µg/L as Ca)	10 µg/L	EPA 200.8
Chromium (µg/L as Cr)	0.25 µg/L	EPA 200.8
Cobalt (µg/L as Co)	0.1 µg/L	EPA 200.8
Copper (µg/L as Cu)	0.07 µg/L	EPA 200.8
Iron (µg/L as Fe <sup>2+</sup> )	4.67 µg/L	EPA 200.8
Lead (µg/L as Pb)	0.05 µg/L	EPA 200.8
Lithium (µg/L as Li)	4.0 µg/L	EPA 200.7

PARAMETER	DETECTION LIMIT (MDL)	METHOD
Magnesium (µg/L as Mg)	2.5 µg/L	EPA 200.8
Manganese (µg/L as Mn)	0.17 µg/L	EPA 200.8
Molybdenum (µg/L as Mo)	0.1 µg/L	EPA 200.8
Nickel (µg/L as Ni)	0.07 µg/L	EPA 200.8
Potassium (µg/L as K)	10 µg/L	EPA 200.8
Selenium (µg/L as Se)	0.22 µg/L	EPA 200.8
Silicon (µg/L as Si)	20 µg/L	EPA 200.7
Silver (µg/L as Ag)	0.25 µg/L	EPA 200.8
Sodium (µg/L as Na)	25 µg/L	EPA 200.8
Strontium (µg/L as Sr)	1.0 µg/L	EPA 200.7
Thallium (µg/L as Tl)	0.05 µg/L	EPA 200.8
Vanadium (µg/L as V)	0.05 µg/L	EPA 200.8
Zinc (µg/L as Zn)	2.5 µg/L	EPA 200.8